Setting Risk-Based Cleanup Goals for Total Petroleum Hydrocarbons (TPH)

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RESEARCH & DEVELOPMENT

Building a scientific foundation for sound environmental decisions

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Presentation Outline

I. Risk-Based Corrective Action Overview

II. Setting risk-based soil cleanup goals for total petroleum hydrocarbons (TPH) to protect ground water

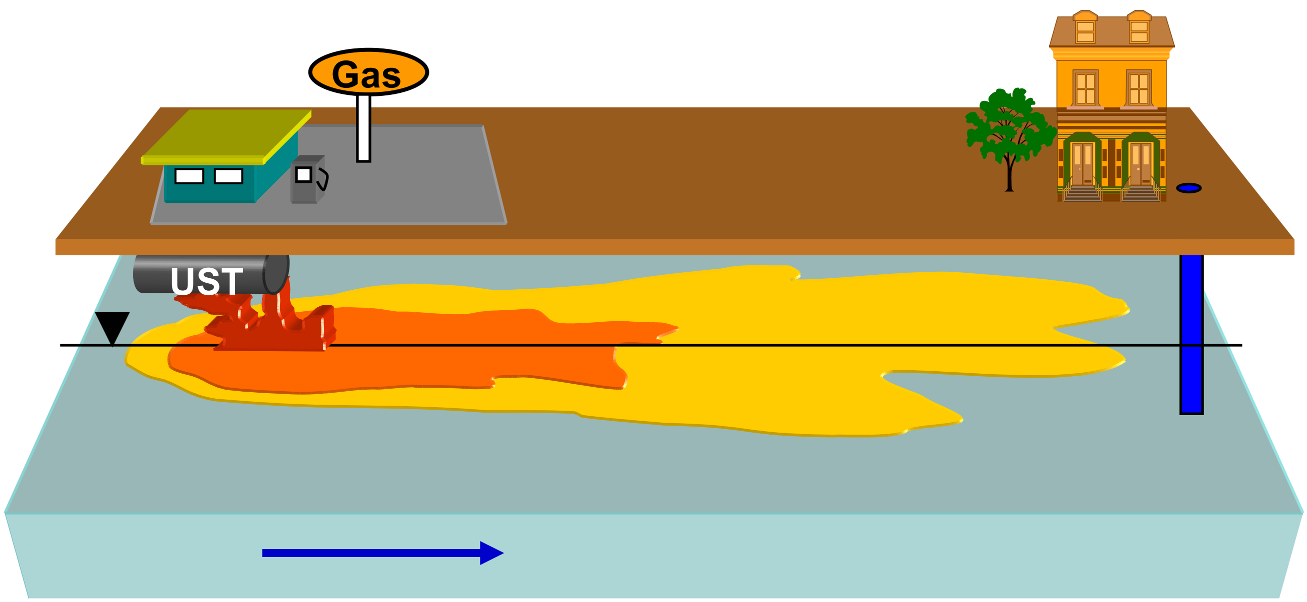
III. Theoretical Issues

IV. Johnston Atoll Case Study and Application

V. Conclusions and Future Research

Cleaning up Petroleum Releases in the United States

- Petroleum releases are considered accidents.
- Responsible parties are required to investigate and clean up contamination.

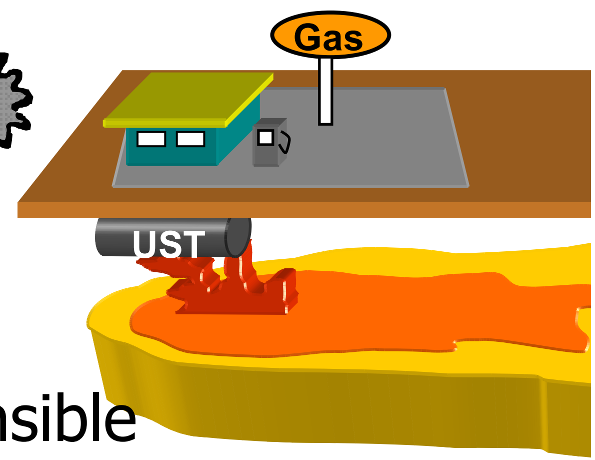


Petroleum Cleanup Process in the United States

- State Regulators set cleanup goals and monitor progress.
- State Funds pay for cleanup.
- Responsible parties perform cleanup.

State Regulators

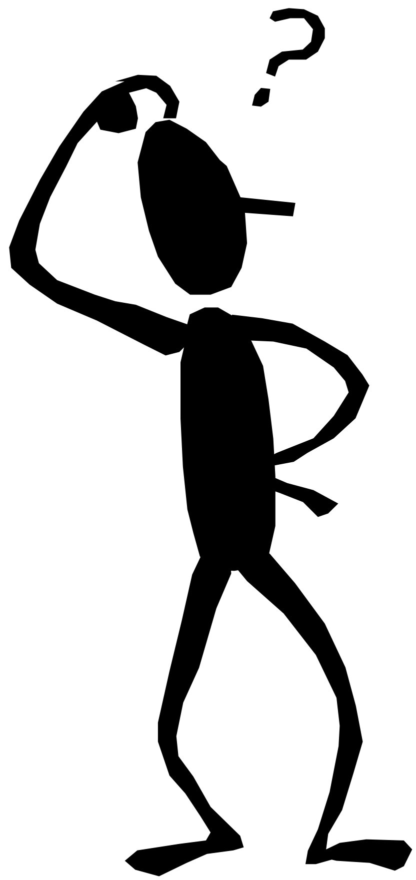
State Cleanup Funds



Responsible Party Cleanup

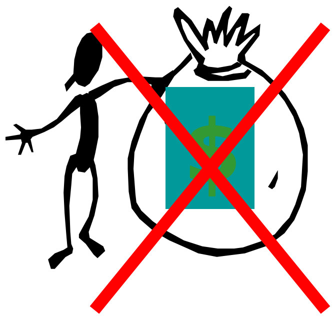
How Clean is Clean?

- How much cleanup is required?
- When can we stop cleaning up?
- What are the cleanup goals?
- Can we restore the site to uncontaminated conditions?



Reality of Cleanup

- We don't have enough money or resources to clean up all petroleum release sites to uncontaminated conditions.
  - State funds have been going bankrupt.
  - Gas stations have gone out of business.
- Economic surrender, we can't do it all.



Cleanup Goals for Petroleum Contamination Have Changed!

- We used to ask,

  "how much contamination can we clean up?"

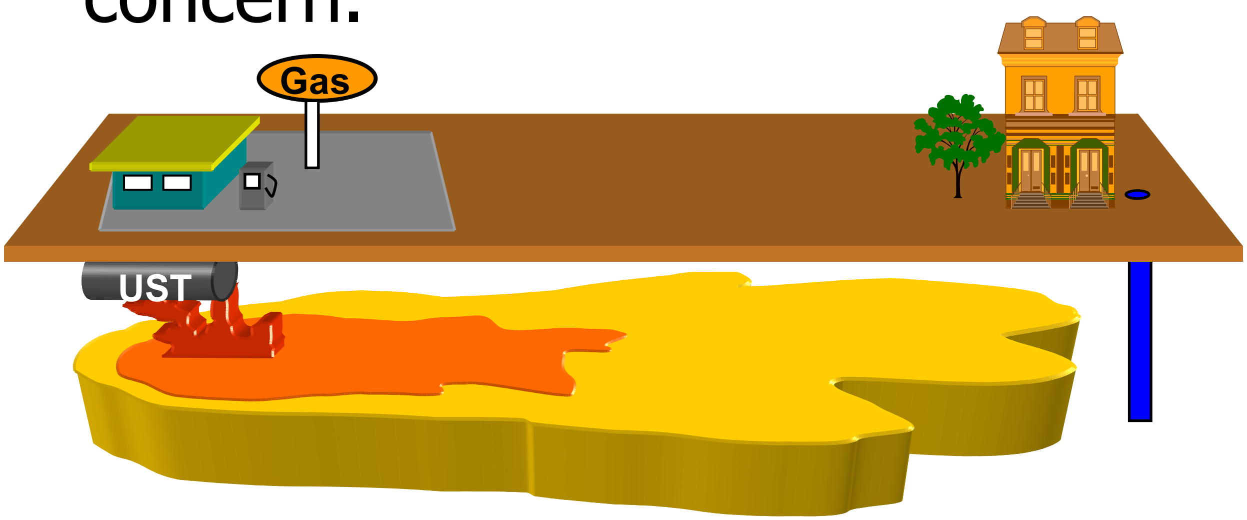
- **Now** we ask,

  "how much contamination can we **safely** leave in place?"

Evaluating Risk

Exposure x Hazard = Risk

- Exposure assessment:
  - Extent of contamination and chemicals of concern.



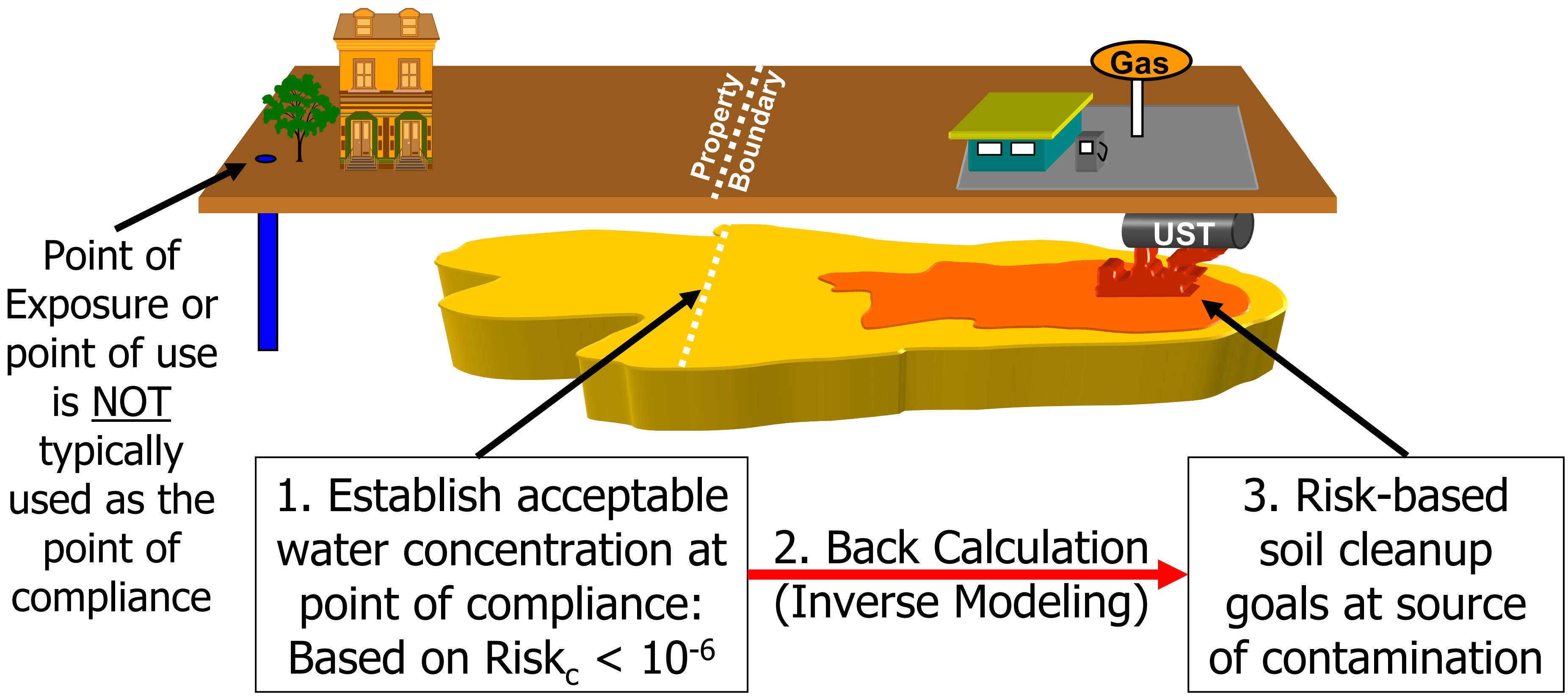
Sources ➡ Pathways ➡ Receptors

Evaluating Risk

Exposure x Hazard = Risk

- Hazard assessment:
  - Chemical dose response data from laboratory studies with animals.
  - Laboratory data extrapolated to humans.
  - Hazard expressed as a cancer slope factor or a reference dose.

- Risk-Based Corrective Action (RBCA) uses models to <u>back-calculate</u> cleanup goals based on allowable risk at point of compliance.



Risk-Based Cleanup Goals
A Tiered Approach

- Tier 1 Risk-Based Screening Levels:
  - Generic/Conservative parameters and assumptions.
- Tier 2 Site-Specific Target Levels:
  - Site specific parameters, conservative assumptions.
- Tier 3 Site-Specific Target Levels:
  - Site specific parameters and assumptions.

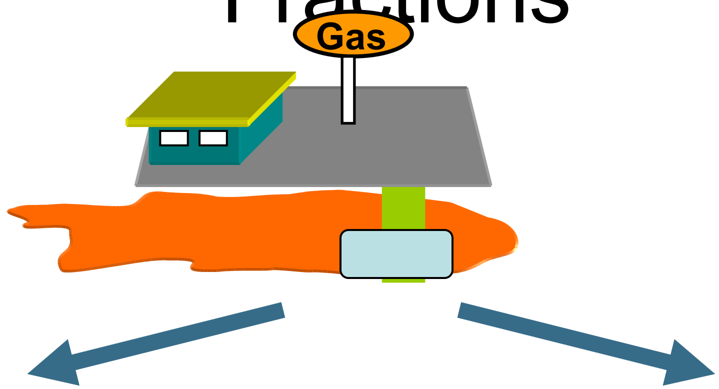
Cleanup Criteria for Petroleum Releases

1) Free product removal to the maximum extent practicable as defined by the implementing agency, and
2) BTEX, oxygenates, and PAH's all below action levels in soil and ground water, and
3) TPH (non-carcinogens) all below action levels in soil and ground water.

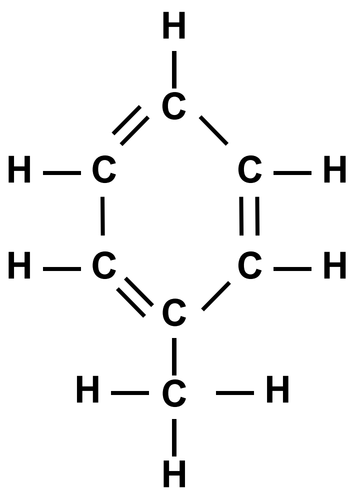
Setting TPH Cleanup Goals for Water

- TPH screening levels calculated separately for: Gasoline, Diesel, Jet Fuel, and Waste Oil
- Generic TPH fractional Composition from TPH criteria working group, WA state, and sampling
- TPH fraction reference doses from EPA NCEA (based on TPHCWG and MA values)
- Default exposure factors from EPA Region 9 Preliminary Remediation Goals (PRGs)

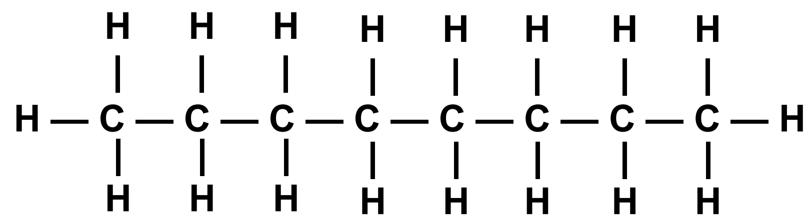
(TPH) Composition: Separate TPH into Fractions



Aromatics

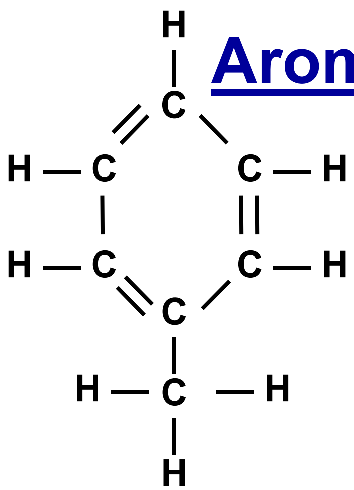


Aliphatics



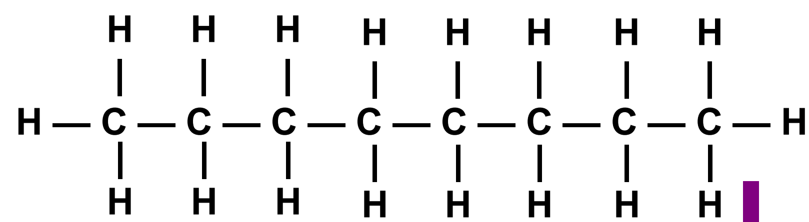
Determining TPH Composition: A fractionated approach

Aromatics



- $>C5\text{-}C6$
- $>C_6\text{-}C_8$
- $>C_8\text{-}C_{10}$
- $>C_{10}\text{-}C_{12}$
- $>C_{12}\text{-}C_{16}$
- $>C_{16}\text{-}C_{21}$
- $>C_{21}\text{-}C_{34}$

Aliphatics



- $>C_8\text{-}C_{10}$
- $>C_{10}\text{-}C_{12}$
- $>C_{12}\text{-}C_{16}$
- $>C_{16}\text{-}C_{21}$
- $>C_{21}\text{-}C_{34}$

Microsoft Excel - weathered gas_NCEA.xls

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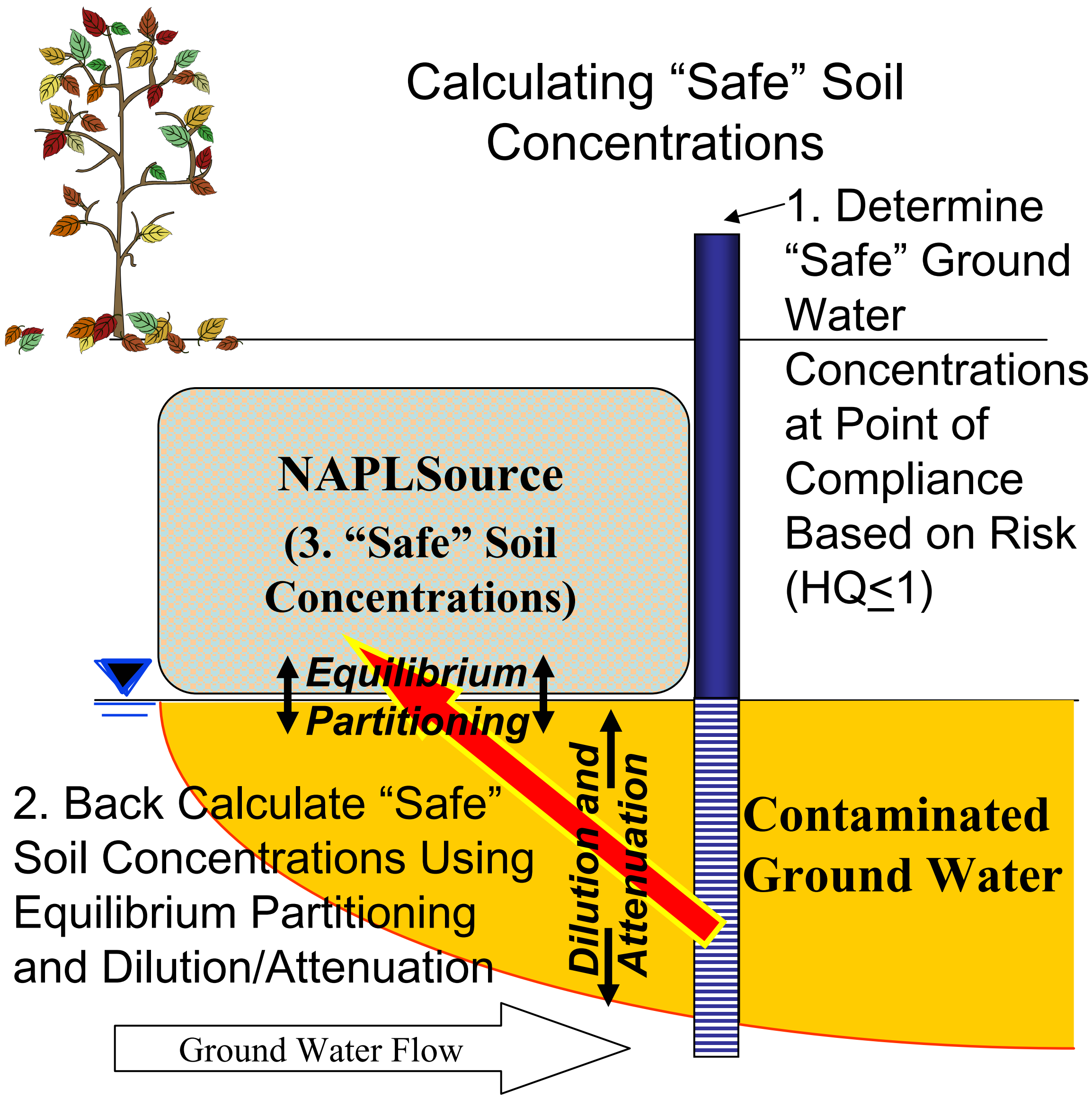
Properties of Chemicals commonly found at Petroleum Contaminated Sites

Note: Please refer to "CLARC VER 3.0 2001" for the source of Database

		Physical-Chemical Properties					Toxicological Properties						
CAS NO	Compound or Petroleum Equivalent Carbon Fraction	Molecular Weight	Aqueous Solubility	Henry's Law Constant	Soil Organic Carbon-Water Partitioning Coef	Liquid Density	Oral Reference Dose	Inhalation Correction Factor	Inhalation Reference Dose	Dermal Absorption Fraction	Gastrointestinal Absorption Conversion Factor	Oral Carcinogenic Potency Factor (with CalEPA's TEF for cPAHs)	Inhalation Carcinogenic Potency Factor (with CalEPA's TEF for cPAHs)
		GFW	*S*	H_{cc}	K_{oc}	ρ	RfD_o	*INH*	RfD_i	ABS_d	*GI*	CPF_o	CPF_i
		mg/mol	mg/l	unitless	l/kg	mg/l	mg/kg-day	unitless	mg/kg-day	unitless	unitless	kg-day/mg	kg-day/mg
	Petroleum EC Fraction												
	AL_EC >5-6	8.100E+04	3.600E+01	3.300E+01	8.000E+02	6.700E+05	5.7	2	5.7	0.03	0.8		
	AL_EC >6-8	1.000E+05	5.400E+00	5.000E+01	3.800E+03	7.000E+05	5.7	2	5.7	0.03	0.8		
	AL_EC >8-10	1.300E+05	4.300E-01	8.000E+01	3.020E+04	7.300E+05	0.1	2	0.085	0.03	0.8		
	AL_EC >10-12	1.600E+05	3.400E-02	1.200E+02	2.340E+05	7.500E+05	0.1	2	0.085	0.03	0.8		
	AL_EC >12-16	2.000E+05	7.600E-04	5.200E+02	5.370E+06	7.700E+05	0.1	1		0.1	0.5		
	AL_EC >16-21	2.700E+05	1.300E-06	4.900E+03	9.550E+09	7.800E+05	2	1		0.1	0.5		
	AL_EC >21-34	4.000E+05	1.500E-11	1.000E+05	1.070E+10	7.900E+05	2	1		0.1	0.5		
	AR_EC >8-10	1.200E+05	6.500E+01	4.800E-01	1.580E+03	8.700E+05	0.02	2	0.05	0.03	0.8		
	AR_EC >10-12	1.300E+05	2.500E+01	1.400E-01	2.510E+03	9.000E+05	0.02	2	0.05	0.03	0.8		
	AR_EC >12-16	1.500E+05	5.800E+00	5.300E-02	5.010E+03	1.000E+06	0.05	1		0.1	0.5		
	AR_EC >16-21	1.900E+05	6.500E-01	1.300E-02	1.580E+04	1.160E+06	0.03	1		0.1	0.5		
	AR_EC >21-34	2.400E+05	6.600E-03	6.700E-04	1.260E+05	1.300E+06	0.04	1		0.1	0.5		
71-43-2	Benzene	7.800E+04	1.750E+03	2.280E-01	6.200E+01	8.765E+05	0.003	2	0.00171	0.0005	0.95	0.055	0.027
108-88-3	Toluene	9.200E+04	5.260E+02	2.720E-01	1.400E+02	8.669E+05	0.2	2	0.114	0.03	1		
100-41-4	Ethylbenzene	1.060E+05	1.690E+02	3.230E-01	2.040E+02	8.670E+05	0.1	2	0.286	0.03	0.92		
	Total Xylenes	1.060E+05	1.710E+02	2.790E-01	2.330E+02	8.752E+05	2	2	0.2	0.03	0.9		
	Total Naphthalenes	1.280E+05	3.100E+01	1.980E-02	1.191E+03	1.145E+06	0.02	2	0.00086	0.13	0.89		
110-54-3	n-Hexane	8.600E+04	9.500E+00	7.400E+01	3.410E+03	6.594E+05	0.06	2	0.057	0.03	0.8		
1634-04-4	MTBE	8.800E+04	5.000E+04	1.800E-02	1.090E+01	7.440E+05	0.03	2	0.86	0.03	0.8		
106-93-4	Ethylene Dibromide (EDB)	1.879E+05	3.400E+03	1.290E-02	6.600E+01	2.170E+06	0.000057	2	0.000057	0.03	0.8	85	0.76
107-06-2	1,2 Dichloroethane (EDC)	9.900E+04	8.520E+03	4.010E-02	3.800E+01	1.253E+06	0.03	2	0.0014	0.03	0.8	0.091	0.091
56-55-3	Benzo(a)anthracene	2.283E+05	9.400E-03	1.370E-04	3.575E+05	1.274E+06		1		0.13	0.89	0.73	0.61
205-99-2	Benzo(b)fluoranthene	2.523E+05	1.500E-03	4.550E-03	1.230E+06	1.300E+06		1		0.13	0.89	0.73	0.61
207-08-9	Benzo(k)fluoranthene	2.523E+05	8.000E-04	3.400E-05	1.230E+06	1.300E+06		1		0.13	0.89	0.73	0.61
50-32-8	Benzo(a)pyrene	2.523E+05	1.620E-03	4.630E-05	9.688E+05	1.300E+06		1		0.13	0.89	7.3	6.1
218-01-9	Chrysene	2.283E+05	1.600E-03	3.880E-03	3.980E+05	1.274E+06		1		0.13	0.89	0.073	0.061
57-70-3	Dibenzo(a,h)anthracene	2.780E+05	2.490E-03	6.030E-07	1.789E+06	1.260E+06		1		0.13	0.89	2.92	2.44
193-39-5	Indeno(1,2,3-cd)pyrene	2.763E+05	2.200E-05	6.560E-05	3.470E+06	1.300E+06		1		0.13	0.89	0.73	0.61

Assumptions of Soil-to-Groundwater Pathway



- No chemical or biological degradation in unsaturated zone;
- Source is infinite, uniformly distributed, extends to the water table;
- Receptor well at edge of source;
- Homogeneity of the soil and aquifer properties;
- Equilibrium Partitioning of chemicals among 3 or 4-phase: Isotherm partitioning model, instantaneous partition;
- Ideal behavior in the NAPL phase as a result of the mixture.

TPH Soil Impacting Ground Water Tiered Approach

Process	Risk-Based Screening Levels	Options for Site-Specific Target Levels
Fuel Composition ↓	• Generic TPH Fractional Compositions	• Site-specific TPH Fractional composition analysis.
Multi-Phase, Multi-Component Partitioning Model ↓	• 3, 4 phase Raoult's Law model (WA DOE) • Ground water RBSLs	•3, 4 phase Raoult's Law Model (WA DOE) • Ground water SSTLs • SPLP analysis. • Site-specific ground water target levels. • lysimeter analysis
Dilution Attenuation Factor ↓	• EPA DAF (1996 SSG) equation with "conservative" parameters.	• EPA DAF equation with site-specific parameters. • API DAFy graphs. • Co-located soil and ground water samples. • Fate and transport modeling
Cleanup Goal	• Soil leaching to ground water Risk-Based Screening Levels.	• Soil leaching to ground water Site-Specific Target Levels

TPH`	Drinking Water (ug/l)	Soil			
		Direct Soil Exposure Soil<10 ft deep (mg/kg)		Subsurface Soil Leaching to Ground Water (mg/kg)	
		Res	Ind	DAF = 1	DAF = 20
Gas (weath)	304 ws	500 on	1,000 on	2 ws	34 ws
JP4 (fresh)	182 ws	500 on	1,000 on	3 ws	75 ws
Diesel (fresh)	328 ws	500 on	1,000 on	18 ws	3,700 rs
Waste Oil	650 ws	500 on	1,000 on	37 ws	10,000 rs

Sources of Data for Preliminary TPH Screening Levels:
Non-carcinogenic toxicity used for calculation of all TPH screening levels. Surface water aquatic life protection values are not presented at this time for TPH. However, no sheen or observable product is allowed on surface waters. Theoretical aqueous solubility limits may be used as a general starting point for determining non-drinking surface water nuisance levels. Odor levels may also play a role in determining non-drinking water nuisance levels.

ws = calculated using TPH risk-evaluation worksheet developed by Washington State (Park and San Juan, AEHS, 2000).
on = based upon odor and nuisance levels (Brewer, personal communication, 2002).
rs = one half of the lower range of residual NAPL concentration in soil (Brost, 2000) intended to prevent the presence of potentially mobile free product.
na = not available.

Issues:

- Issue:
  - Limited data on TPH fractional composition
- Resolution:
  - EPA gas sampling and fractional analysis?
  - Data from industry?

- Issue:
  - Model is sensitive to DAF
- Resolution:
  - Consider range of DAFs
  - Further evaluate methods for determining DAF
  - Attenuation factor added to EPA DAF?

$$DAF = \left(1 + \frac{Kid}{IL}\right)\exp\left[-kt_R\right] \qquad t_R = R\frac{L}{Ki}$$

Issues:

- Issue:
  - – Fresh versus weathered toxicity
- Resolution:
  - – EPA Lab studies to simulate weathering of TPH fractions

Issues:

- Proposed approach calculates a remedial goal for current conditions and current risk, does not evaluate historic or long term risk to original TPH mixture.
- Hazard Index of TPH plus Hazard Index of remaining BTEX, oxygenates, and PAH's is unknown and may exceed HI $\leq$ 1

Case Study:
Johnston Atoll Project

Developing Site-Specific Eco-Risk Based Cleanup Goals for TPH Contamination at Johnston Atoll

Background

- JACADS (Johnston Atoll Chemical Agency Disposal System) Facility
  - 800 miles southwest of Hawaii
  - Incineration/destruction of 4 million pounds of chemical agents and weapons
  - Incineration completed November 2000
  - Multiple contaminants including petroleum

Background

- September 2002, EPA approved the Army's Revised Closure Plan
  - Green light to proceed with facility closure
  - Return JACADS to conditions safe for people, birds and marine life
- Closure plan includes petroleum hydrocarbon remediation

USFWS/Gerald Ludwig

Site-Specific Eco-Risk Based TPH Cleanup Goals

- Cleanup criteria:
  - No mobile free product
  - Individual compound (BTEX and PAH) concentrations below cleanup goals
  - TPH below cleanup goals
- Ecosystem is the principle receptor:
  - Discharge of ground water to marine receptors
  - Direct avian exposure to contaminated soil

Site-Specific Eco-Risk Based TPH Cleanup Goals

- The challenge:
  - Develop site-specific eco-risk based cleanup goals for TPH in soil and ground water
    - Ground water cleanup goals to protect marine environment
    - Soil cleanup goals to protect ground water
    - Soil cleanup goals to protect direct eco-receptor exposure
    - Soil cleanup goals to protect direct human exposure
    - Soil cleanup goals to prevent product migration

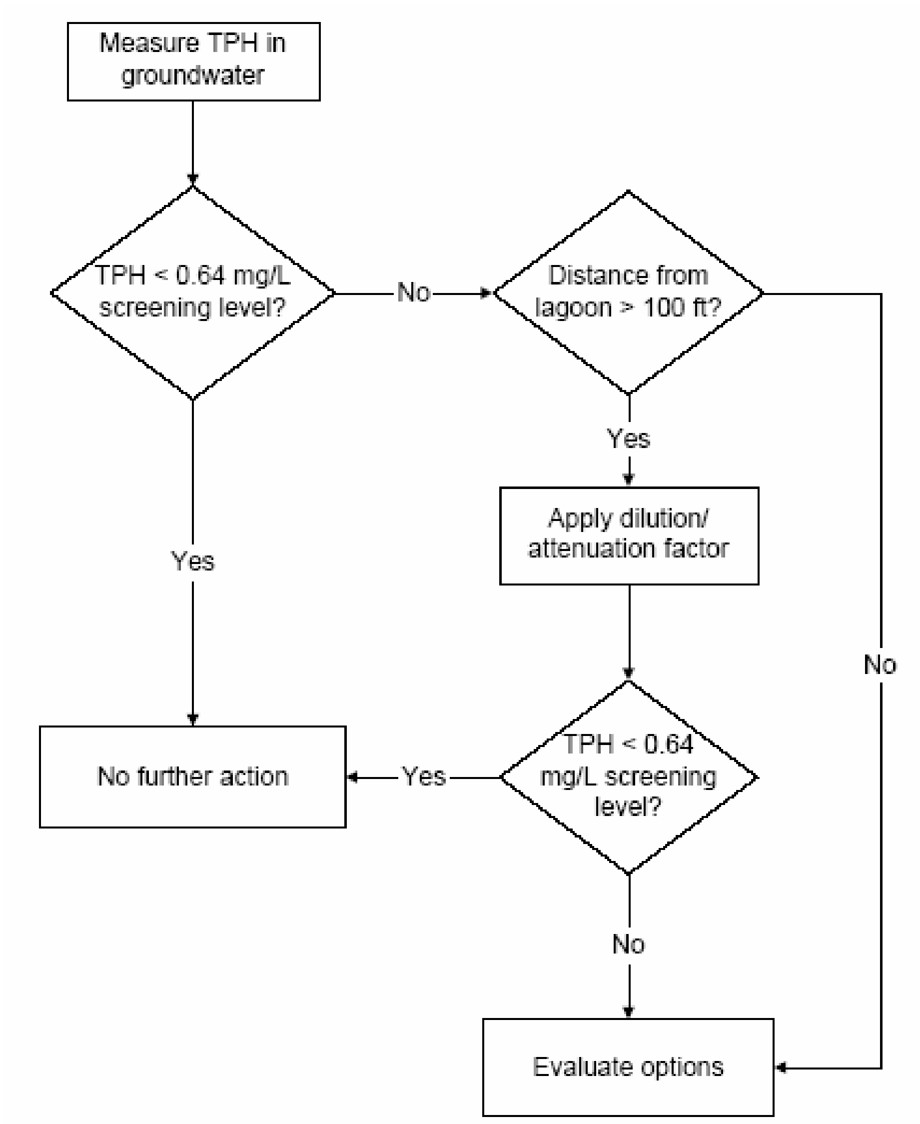
Groundwater Evaluations

- Discharge of Groundwater to Marine Environment (Lagoon)
- Ground Water action level of 0.640 mg/l adapted from studies in San Francisco Bay
  - Mysidopsis bahia, invertebrate
  - The toxicity test used chronic exposure
  - Endpoint included sub lethal effect (growth)

Groundwater Evaluations

- GW concentration data should be adjusted using a Dilution Attenuation Factor (DAF) to estimate GW concentrations at the shoreline.
- Dilution attenuation factor:
  - DAF = 1 for locations ≤ 100 ft from shoreline
  - DAF = distance/100 for locations > 100 ft

Decision Process for GW TPH



Identifying Site-Specific Soil Exposure Pathways

- Goals to Protect Direct Eco-Receptor Exposure:
  - Fractional analysis of TPH to determine composition
  - Eco-risk evaluated using fractional toxicity
- Goals to Protect Direct Human Exposure:
  - Fractional analysis of TPH to determine composition
  - Human risk evaluated using fractional toxicity
- NAPL Mobility Exposure Goals:
  - Residual non-aqueous phase liquid (NAPL) saturation calculated for Johnston Atoll soils

Identifying Site-Specific Soil Exposure Pathways (cont.)

- Goals to Protect Ground Water
  - Based upon site-specific synthetic precipitation leaching potential test
    - “worst case” leaching potential
  - Relatively low solubility compounds
  - Site specific Cleanup goal of 30,000 mg/kg in soil would not be expected to impact ground water above 0.640 mg/L
  - Previous default TPH action levels was 5,000 mg/kg in subsurface soil (not risk based, nor site specific)

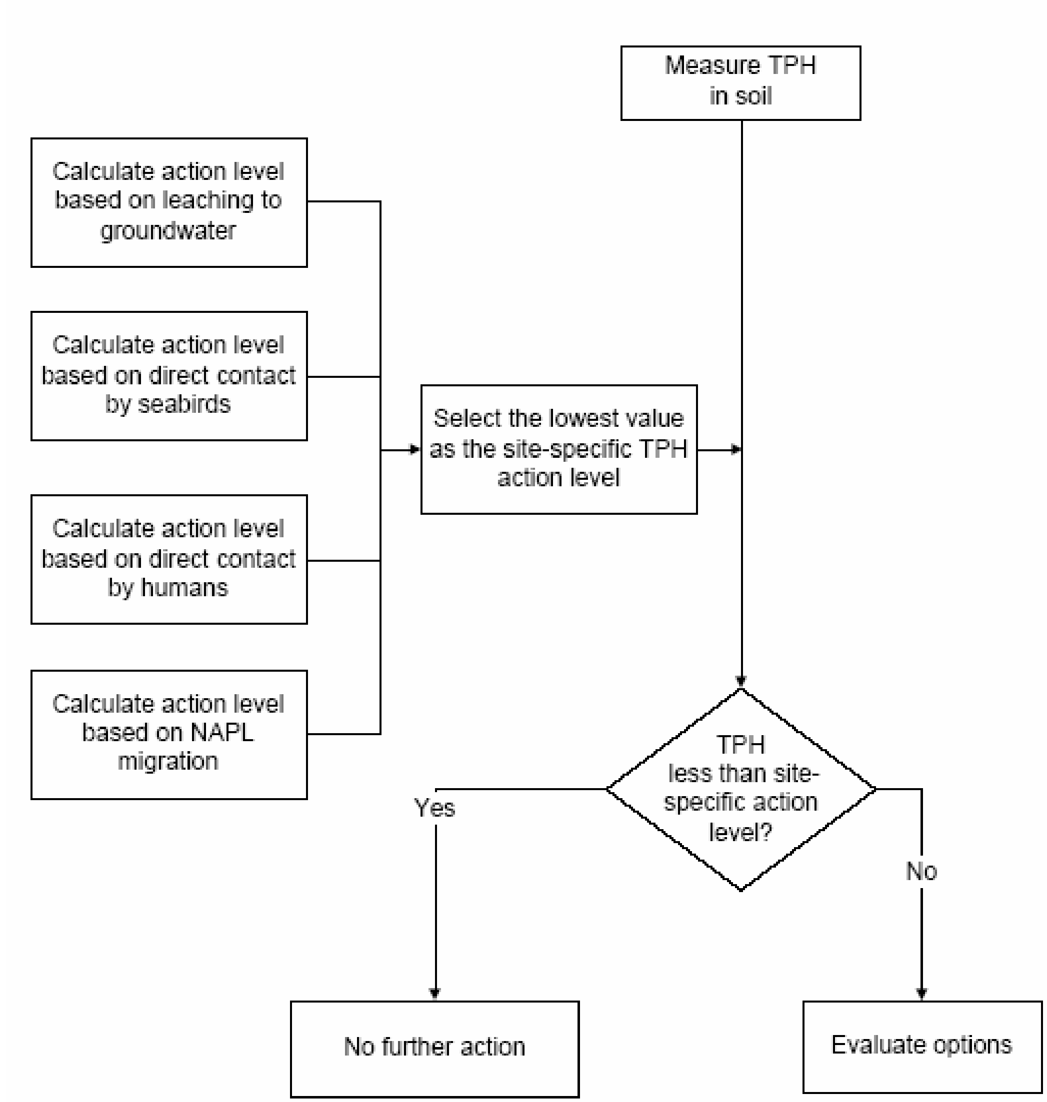
Site-Specific Soil Action Levels

- Multiple exposure pathways:
  - Groundwater protection 30,000 to 40,000 mg/kg
  - Direct soil contact by eco-receptors 73,000 to 161,000 mg/kg
  - Direct soil contact by human receptors.33,000 to 71, 000 mg/kg
  - Free product mobility 13,074 to 22,560 mg/kg

Soil Action Levels

- Soil Action level = 17,181 mg/kg based upon mobility limits (previously 2,000-5,000 mg/kg for surface/subsurface)

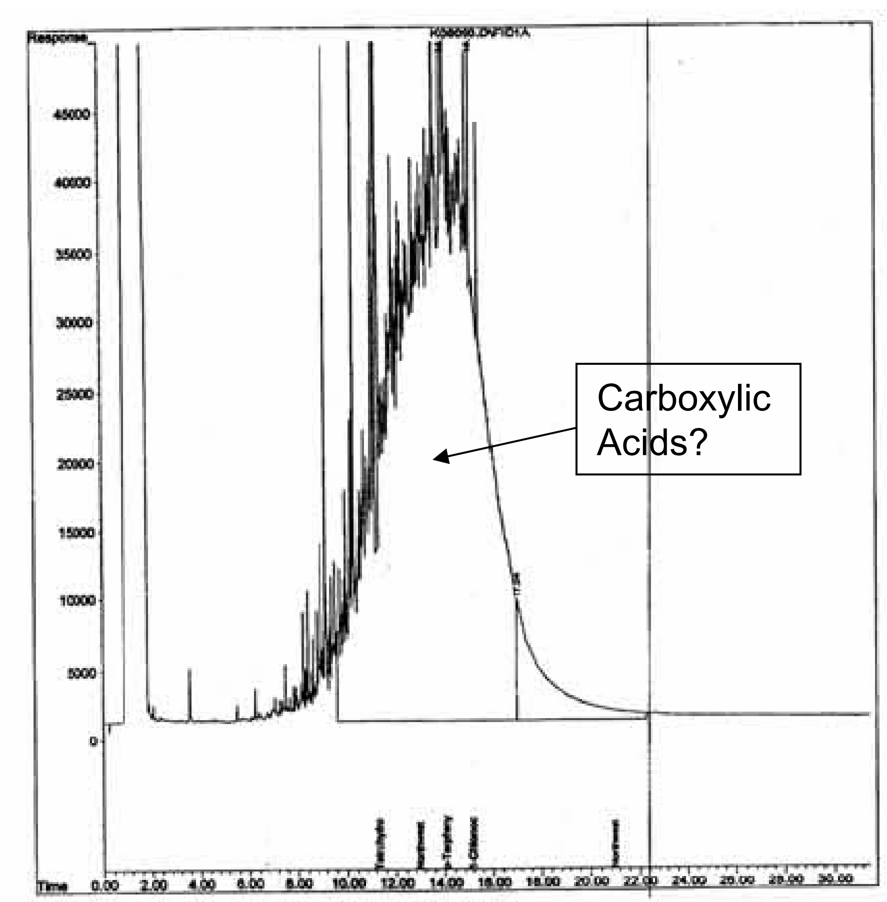
Decision Process for Soil TPH



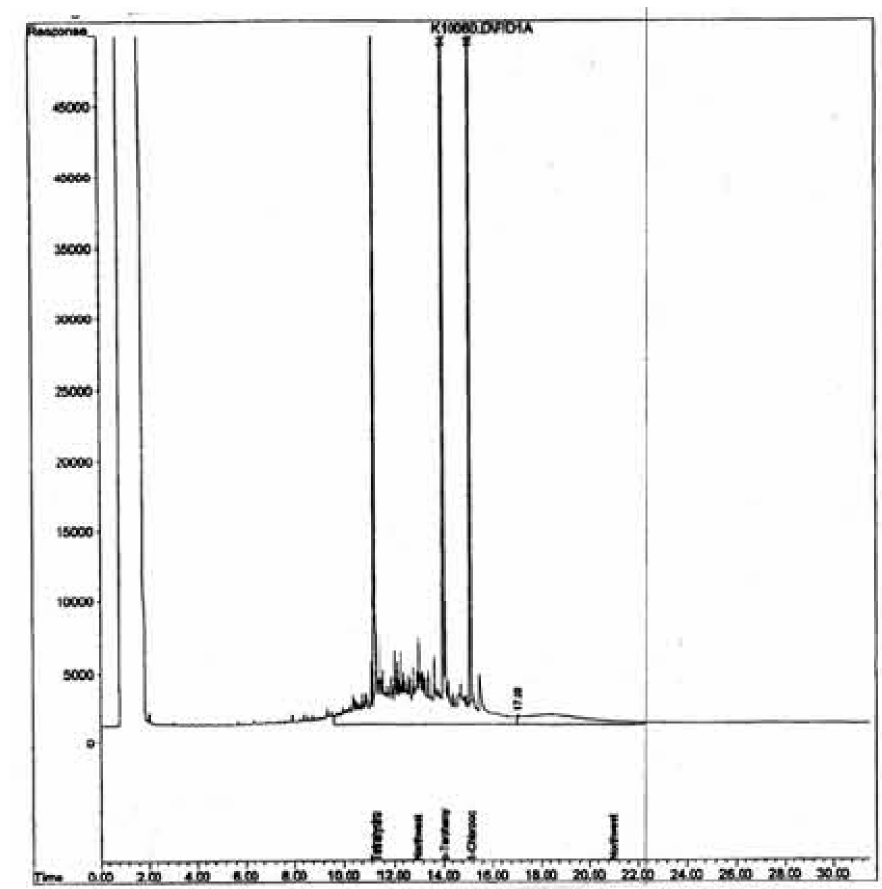
Other Issues

- Silica gel cleanup
- Disagreement between TPH concentrations measured fractional analysis and 8015
- Dilution Attenuation Factor

Silica Gel Cleanup



NWTPH-Dx without
Silica Gel Cleanup



NWTPH-Dx with Silica
Gel Cleanup

Disagreement Between TPH Analytical Methods

Sample	Units	Distance to Lagoon (ft)	*Dilution Attenuation Factor (distance/100)*	Total TPH A divided by DAF	Total TPH B (SGCU) divided by DAF	Total TPH C (fractionation) divided by DAF
FW-MW03D-1103	mg/L	1114	*11.14*	0.164	0.023	0.023
SWM-MW20-1103	mg/L	701	*7.01*	0.231	0.124	0.096
SWM-MW21-1103	mg/L	638	*6.38*	0.272	0.063	0.057
SWM-MW22-1103	mg/L	957	*9.57*	0.182	0.087	0.058
T49-FD1-1103[a]	mg/L	386	*3.86*	**3.060**	**1.036**	0.150
T49-MW15-1103	mg/L	386	*3.86*	**1.915**	0.515	0.140
T49-MW05-1103	mg/L	30	*1*	0.498	0.213	0.227
T49-MW06-1103	mg/L	306	*3.06*	0.444	0.487	0.332
T49-MW07-1103	mg/L	280	*2.8*	**1.940**	0.118	0.149

Notes:

[a] Field duplicate of sample T49-MW15-1103.

Bold and shading indicates value is greater than 0.64-mg/L action level.
Total TPH A = Sum of detected NWTPH-Gx, NWTPH-Dx diesel, and NWTPH-Dx lube oil
Total TPH B = Sum of detected NWTPH-Gx, NWTPH-Dx SGCU diesel, and NWTPH-Dx SGCU lube oil
Total TPH C = Sum of NWTPH-VPH and NWTPH-EPH.

mg/L = milligram per liter
SGCU = silica gel cleanup
TPH = total petroleum hydrocarbons

Conclusions

- Successfully developed site specific risk-based TPH clean up goals
- Helped move site toward closure safely and quickly
- Created model for future applications
- Identified questions for additional investigations

Future Work and Research Needs

- Further evaluation of DAF
- More lab experiments for solubility of TPH fractions
- Nationwide sampling and analysis of gasoline composition
- Combining lab and field data to develop generic fuel compositions
- Combining lab and field data to risk-based cleanup goals